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# 1    **Production of phosphorene nanoribbons**

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13

14    **Phosphorene is a mono-elemental two-dimensional (2D) material with outstanding,**  
15    **highly directional properties and a thickness-tuneable band gap<sup>1-8</sup>. Nanoribbons**  
16    **combine the flexibility and unidirectional properties of 1D nanomaterials, the high**  
17    **surface area of 2D nanomaterials and the electron-confinement and edge effects of both.**  
18    **Their structures can thus offer exceptional control over electronic bandstructure, lead**  
19    **to the emergence of novel phenomena and present unique architectures for**  
20    **applications<sup>5,6,9-24</sup>. Motivated by phosphorene's intrinsically anisotropic structure,**  
21    **theoretical predictions of the extraordinary properties of phosphorene nanoribbons**  
22    **(PNRs) have been rapidly emerging in recent years<sup>5,6,12-24</sup>. However to date, discrete**  
23    **PNRs have not been produced. Here we present a method for creating quantities of high**  
24    **quality, individual PNRs via ionic scissoring of macroscopic black phosphorus crystals.**

25 The top-down process results in stable liquid dispersions of PNRs with typical widths of  
26 4 to 50 nm, predominantly single layer thickness, measured lengths up to 75  $\mu\text{m}$  and  
27 aspect ratios of up to  $\sim 1000$ . The nanoribbons are atomically-flat single crystals, aligned  
28 exclusively in the zigzag crystallographic orientation. The ribbon widths are  
29 remarkably uniform along their entire length and they display extreme flexibility.  
30 These properties, in conjunction with the ease of down-stream manipulation via liquid-  
31 phase methods, now enable the search for predicted exotic states<sup>6,12-14,17-19,21</sup> and an  
32 array of applications where PNRs have been widely predicted to offer transformative  
33 advantages, ranging from thermoelectric devices to high-capacity fast-charging  
34 batteries and integrated high-speed electronic circuits<sup>6,14-16,20,23,24</sup>.

35

36 Phosphorene's anisotropic properties, including for electron, thermal and ionic transport,  
37 derive from its atomic structure where the atoms are arranged in corrugated sheets with two  
38 different P-P bond lengths (Fig. 1a)<sup>1-8</sup>. Calculations predict that PNRs can possess enhanced  
39 characteristics compared with phosphorene and that their electronic structure, carrier  
40 mobilities and optical and mechanical properties can be tuned by varying the ribbon width,  
41 thickness, edge passivation, and by introducing strain or functionalization<sup>6,12-14,20,22-24</sup>.  
42 Additionally, there have been numerous predictions of exotic effects in PNRs, including the  
43 spin-dependent Seebeck effect<sup>17</sup>, room temperature magnetism<sup>6,21</sup>, topological phase  
44 transitions<sup>18</sup>, large exciton splitting<sup>14</sup> and spin density waves<sup>19</sup>. These results have led to  
45 suggestions of unique capabilities of PNRs in a number of applications such as thermoelectric  
46 devices<sup>6,23</sup>, photocatalytic water splitting<sup>15</sup>, solar cells<sup>14</sup>, batteries<sup>6,24</sup>, electronics<sup>6,20,22</sup> and  
47 quantum information technologies<sup>14</sup>.

48

49 The production of nanoribbons of any material is a major challenge. Top-down processes  
50 generally fail to deliver the narrow and uniform widths, crystallinity and crystallographic  
51 alignment required for well-defined control of the nanoribbon's electronic structure<sup>6,9,11,20</sup>.  
52 Such control has been demonstrated by polymerisation of molecular precursors to produce  
53 graphene nanoribbons (GNRs)<sup>9</sup>, however, this and many other methods developed for  
54 GNRs<sup>10,11</sup> are not currently transferable to phosphorene, an issue compounded by  
55 phosphorene's air-sensitivity and chemical reactivity<sup>6</sup>. Attempts to fabricate PNRs have been  
56 so far limited to etching of multi-layer black phosphorus (BP), the 3D layered parent  
57 structure of phosphorene (Fig. 1a)<sup>5,16,25</sup>. Electron-beam sculpting produces nanoscale  
58 constrictions over limited ( $< 15$  nm) lengths rather than isolated nanoribbons<sup>16</sup>. Alternatively,  
59 e-beam lithography has, to date, only produced ribbons with minimum widths of  $\sim 60$  nm and  
60 heights of  $\sim 3$  nm (Ref 25) meaning their band gaps and electronic properties are close to  
61 those of bulk BP<sup>2,3,14,20,22</sup>. Such lithography also relies on first exfoliating and then  
62 crystallographically aligning BP, limiting the scalability essential for many applications.

63

64 Our method for PNR production follows a two-step process. First, macroscopic crystals of  
65 bulk black phosphorus are intercalated with lithium ions via a low temperature, ammonia-  
66 based method (Li:P molar ratio 1:8). The resulting compound is then immersed in an aprotic  
67 solvent and mechanically agitated producing stable liquid dispersions of PNRs (Fig. 1b,  
68 inset). A schematic of the process is shown in Extended Data Fig. 1 and further details are  
69 given in the Methods. The mechanism for ribbon formation is discussed below. For  
70 characterisation the PNRs were drop-cast from liquid dispersion onto graphite substrates or  
71 Transmission Electron Microscopy (TEM) grids.

72

73



74 Following deposition, the TEM grids were ubiquitously covered in ribbons. Example  
75 micrographs are displayed in Fig. 1b and a gallery of TEM images is shown in Extended Data  
76 Fig. 2, which presents densely packed heterogeneous PNRs and isolated high aspect ratio  
77 ribbons with widths  $< 5$  nm. From TEM data, the length and width of 940 individual ribbons  
78 were measured (Methods), plotted as a scatter plot in Fig. 1c. The average length of these  
79 ribbons is 690 nm, average width 30 nm; 33% of the ribbons are narrower than 10 nm.  
80 Histograms of the width and lengths with axes corresponding to the dashed rectangle in the  
81 scatterplot are also shown in Fig. 1c.

82

83 Selected Area Electron Diffraction (SAED) was used to investigate the crystallinity of the  
84 deposited ribbons. The TEM micrograph in Fig. 1d contains a ribbon of length  $\sim 11$   $\mu\text{m}$ . The  
85 abrupt changes of the ribbon direction are a result of it twisting and folding onto the  
86 continuous carbon TEM grid upon deposition. SAED patterns were taken at six different  
87 locations along this ribbon (Fig. 1e and Extended Data Fig. 3) and each match the in-plane  
88 black phosphorus diffraction pattern (Methods). Moreover, comparing the alignment of the  
89 individual reciprocal space SAED patterns with their corresponding real space images reveals  
90 that the long ribbon axis is always oriented in the zigzag crystallographic direction (as  
91 indicated by red arrows in Figs. 1a, 1d, 1e, Extended Data Fig. 3). Equivalent measurements  
92 were performed on over 40 PNRs and in all cases SAED confirmed that the PNRs were  
93 crystallographically intact along their length and zigzag edge-aligned, with no other  
94 alignment observed.

95

96 Ribbon folding upon drying could be reduced by using holey carbon TEM grids. In this case,  
97 the PNRs were found to be extraordinarily flexible and could twist, loop and coil around the  
98 carbon substrate as seen in Figs. 1f, 1g and Extended Data Fig. 2c. This flexibility, combined

with their low TEM contrast, indicates that the PNRs are only a few layers thick, though only in rare cases could TEM be used to determine their height. Fig. 1g shows a high-resolution TEM (HRTEM) image taken through a ribbon fold. For this ribbon, the intact atomic corrugations of the BP lattice are visible and seven distinct layers can be counted. HRTEM taken through the flat part of the ribbon (Fig. 1h) reveals the expected, in-plane BP lattice, which give sharp spots in the associated Fast Fourier Transform.

To accurately measure the ribbon heights, we used high-speed atomic force microscopy (HS-AFM) to obtain height-calibrated data over large areas of the substrate (Methods). In all cases, the PNRs' heights closely matched an integer number of layers of black phosphorus. Fig. 2a presents example HS-AFM images of 1 to 5 layer PNRs in 3D view and the same data viewed through the length of each ribbon. These data demonstrate the remarkable height uniformity of the PNRs along their length, showing no fragments or residual species commonly found on AFM images of liquid exfoliated nanomaterials. To determine the PNR heights and roughnesses with greater statistical accuracy, over 130 PNRs of up to five layers thick were imaged and the heights of every pixel in each ribbon extracted and are plotted as normalised histograms in Extended Data Fig. 4 (Methods). Gaussian fits to the histograms determine the heights of 1, 2, 3, 4 and 5 layer PNRs to be 0.52, 1.04, 1.57, 2.09 and 2.74 nm respectively. Notably, the overall roughnesses, which corresponds to the standard deviation of the PNR heights, taken from fits to all measurements in each case (Methods, Extended Data Fig. 4) are comparable to the equivalent data for the naked, atomically-flat graphite substrate.

The PNR layer number distribution within a typical sample was estimated by analysing all the ribbons deposited within a 300 x 300  $\mu\text{m}$  square region on the HOPG substrate plotted in

Fig. 2b (Methods). These data show the majority of the PNRs are monolayer (~65%); 84% were trilayer or fewer.

A high degree of width uniformity is required for nanoribbons with precisely defined electronic character<sup>6,9,11,20</sup>. Fig. 2d displays a ~3  $\mu\text{m}$  section from a single layer PNR. This ribbon's width was measured at over 2,300 points along its length (Methods), plotted as a histogram in Fig. 2c. A Gaussian fit determines the mean width to be 10.3 nm with a standard deviation of 0.7 nm (Methods).

HS-AFM also enabled the study of the longest PNRs. Fig. 2e is a composite HS-AFM image of a ribbon greater than 75  $\mu\text{m}$  in length, alongside the corresponding gradient image (Methods) to highlight the PNR position given its extreme aspect ratio; the ribbon is more clearly visualised in Supplementary Video 1. This ribbon branches at several points along its length, a phenomenon occasionally found for the longer ribbons (see also Extended Data Fig. 5). Line profiles (Extended Data Fig. 5) at the branching points (Fig. 2e, left) reveal that the split is due to the multilayer ribbon having bifurcated via self-cleaving. The extreme flexibility of the PNRs is again demonstrated; the ribbons both follow the underlying graphite steps, or other PNRs when laying on top one another (Fig. 2e, right) with sub-nanometre conformity.

We now discuss the mechanism of PNR formation. Control experiments (Methods) confirm that the lithium intercalation step is essential for ribbon production. Metal-intercalation of black phosphorus (BP) is not fully understood since attempts typically result in both intercalation and other phosphorus-containing compounds, and a well-defined interlayer increase, typical for intercalation compounds, is not found<sup>26</sup> (Methods). Recent HRTEM

experiments on BP intercalation<sup>27</sup> have confirmed the predicted extraordinarily rapid alkali metal ion diffusion along the zigzag direction<sup>8</sup>. This process results in the metal atoms forming ‘stripes’ along the corrugated channels of the BP crystal upon initial doping<sup>27</sup>. The strain between the intercalated and unintercalated regions, combined with high local electron doping, can cause the longer P-P bonds to break and thus crack formation in the zigzag direction<sup>8,26-28</sup>. These findings are consistent with our own observations. Figs. 3a-c presents TEM data capturing the three stages of ribbon formation: Fig. 3a shows a Li-intercalated BP (Li-BP) flake exhibiting cracks along only one direction; Fig. 3b, a flake splitting along these cracks; eventually leading to the formation of isolated ribbons upon mechanical agitation (Fig. 3c). Alternatively, the PNRs were found to spontaneously dissolve from Li-BP crystal, that is, without any agitation or reaction, similar to other nanomaterials when negatively charged by intercalation<sup>29</sup>. The spontaneously dissolved PNRs were found to have greater average width and length than those formed by mechanical agitation (Extended Data Fig. 6).

Applying an electric field to a PNR liquid dispersion (Methods), via Pt-coated electrodes, demonstrates the negative charge on the PNRs in solution, since they are found to electroplate only onto the metallic parts of the positive electrode, as confirmed by Raman and XPS mapping (Fig. 3d-f, Extended Data Fig. 7, Methods). The PNR solutions were found to be remarkably stable in inert atmosphere with UV/Vis absorption measurements, demonstrating less than a 1.5% decrease in absorbance over 50 days (Extended Data Fig. 10, Methods).

We therefore propose the following formation mechanism. The highly directional and rapid intercalation of metal ions leads to breaking of longer P-P bonds along the zigzag direction, resulting in ribbon-like fragments within the Li-BP crystal. The ion intercalation negatively

charges the layers, meaning that when placed in an appropriate polar solvent (Methods) the anionic PNRs can dissolve; agitation (sonication or stirring) can encourage the individual ribbons to fully separate. This mechanism explains the remarkable width uniformity, the exclusive zigzag alignment, the smooth (fragment free) surfaces, and the prevalence of monolayer PNRs (alternative liquid exfoliation strategies for BP, i.e. routes without intercalation, typically result in predominantly greater thickness sheets<sup>7</sup>).

The collective optical properties of PNRs deposited on graphite were investigated with Raman and Photoluminescence (PL) spectroscopies (Methods). All Raman spectra (example Fig. 3g) exhibit peak positions, widths and relative intensities (Extended Data Fig. 9) consistent with mechanically exfoliated few layer phosphorene, though with additional peaks (Fig. 3g inset) attributable to the expected symmetry-breaking at the ribbon edges<sup>30</sup>. The PNRs luminesce emitting at  $\sim 1.4$  eV (Extended Data Fig. 9, Methods) consistent with predictions that single layer PNRs are semiconductors with optical gaps in this energy range<sup>14</sup>. Core-loss electron energy loss spectroscopy (EELS) at the P  $L_{2,3}$  edge from an individual PNR (Extended Data Fig. 3) demonstrates that the P environment is similar to measurements and calculations of pristine BP showing no oxidation<sup>31</sup>; low-loss EELS (Extended Data Fig. 3) resolves the expected plasmon peak at  $\sim 19$  eV, as measured in bulk BP and few layer phosphorene<sup>31</sup>. Notably, these features are sensitive to oxidation and defect concentration<sup>31</sup> and thus further confirm the structural integrity of the PNRs. However, though stable in an inert atmosphere (in solution and once deposited on a substrate), a multi-technique stability study (Methods, Extended Data Fig. 10) reveals that deposited PNRs gradually oxidise upon air exposure, similar to 2D phosphorene<sup>6</sup>.

The PNRs produced have a remarkable range of widths, aspect ratios and lengths when compared with nanoribbons of other materials, while crucially maintaining high width uniformity. Significantly, the production method is scalable, and the stable liquid dispersions permit the PNRs to be efficiently manipulated into thin films, membranes, composites, electrodes, heterostructures and devices<sup>7,29</sup>. Zigzag PNRs have been predicted to exhibit a variety of novel effects<sup>14,17-19,21</sup> and this alignment means that the fast transport of ions is along the ribbon axis, important for battery applications<sup>8,24</sup>. For (opto)electronic devices PNRs are predicted to offer band-gaps ranges distinct from other 2D materials and high hole mobilities<sup>20,25</sup>. For these applications bifurcations present unique possibilities for fabricating seamless transitions for integrated electronics.

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 292 version of the paper. Correspondence should be addressed to C.A.H. (c.howard@ucl.ac.uk)  
 293

294 **Author Contributions** M.C.W. discovered the PNR production method and produced the  
 295 samples. M.C.W. developed the production method with input from P.L.C., N.T.S. and  
 296 C.A.H. The HS-AFM measurements were performed and analysed by L.P., O.D.P., F.R-P.  
 297 and M.C.W. L.P. wrote the automated HS-AFM ribbon detection and step height  
 298 measurement algorithms. F.R-P. wrote the automated ribbon width measurement algorithm  
 299 and produced the HS-AFM movie. M.C.W. and V.T. performed and analysed the TEM.  
 300 T.S.M., M.C.W. and C.A.H. performed the electroplating, T.S.M. collected and analysed the



XPS data, C.A.H. collected and analysed the Raman and PL data with input from S.P.B. P.L.C measured the UV/vis absorption spectra. M.C.W. and C.A.H. planned the experiments and wrote the paper with input from all the authors. C.A.H. directed the project.

**Fig. 1 | TEM characterisation of PNRs.** **a**, The crystal structure of black phosphorus. **b**, TEM micrograph (scale bar 10  $\mu\text{m}$ ) of PNRs drop-cast from liquid dispersion shown in inset. **c**, (left) Scatter plot of PNR length as a function of width taken from 940 PNRs measured using TEM, (right) histograms of the associated aspect ratio (top), and the widths (middle) and lengths (bottom) corresponding to the dashed rectangle on the scatter plot. **d**, composite TEM micrograph of an  $\sim 11\ \mu\text{m}$  PNR on a continuous carbon TEM grid that has folded upon drying, red arrows indicate the zigzag crystallographic direction determined from SAED (Methods) (scale bar 1  $\mu\text{m}$ ), dashed boxes demarcate the different images from which the composite is produced. **e**, SAED pattern corresponding to the blue box in **d** (scale bar 5  $\text{nm}^{-1}$ ). **f**, Micrographs of PNRs, deposited on holey carbon TEM grids, displaying extreme flexibility: (left) composite TEM micrograph of a twisted ribbon with radius of curvature  $5.5 \pm 0.5\ \text{nm}$  at the region marked by blue arrows and (right) High Angle Annular Dark Field (HAADF) image of a PNR (scale bar, both 500 nm). **g** High Resolution TEM (HRTEM) micrograph of a folded PNR, outlined by yellow dashes for visibility (scale bar 500 nm); a high magnification image through bend (top right), corresponding to the dashed box and showing seven distinct BP layers (scale bar 2 nm), and line cut perpendicular to the layers showing the two P atom planes in BP indicated by red and blue lines. **h**, HRTEM micrograph through the dashed box from the flat region of the ribbon in **g**, showing the ordered atomic lattice with associated FFT (bottom right) and zoom (top right) (scale bars 10 nm, inset 1 nm, FFT  $10\ \text{nm}^{-1}$ ) peaks in the FFT are indexed in Extended Data Fig. 3.

**Fig. 2 | AFM characterisation of PNRs.** **a**, HS-AFM images of 1.5  $\mu\text{m}$ -long sections of PNRs with heights corresponding to 1-5 phosphorene layers, in 3D view (top) and the same dataset (bottom) rotated with the view direction through the ribbon length (scale bar 500 nm). **b**, Histogram of the PNR layer number for 230 ribbons deposited within a  $300 \times 300\ \mu\text{m}$  area of substrate. **c**, Histogram of the widths of the PNR shown in **d** measured at 2,300 points along its length (error bars) and Gaussian fit to this data (solid line). **d**, HS-AFM micrograph of a monolayer PNR (scale bar 500 nm) **e**, Large area, composite HS-AFM micrograph of a  $>75\ \mu\text{m}$  long PNR (scale bar 10  $\mu\text{m}$ ), plotted alongside gradient image (Methods) for clarity. Zoomed sections corresponding to the dashed boxes on the central image are also shown demonstrating: bifurcations (top left) and a junction of two PNRs crossing (bottom right) (scale bars both 500 nm).

**Fig. 3 | PNR formation (a-f) and Raman spectroscopy (g) of deposited PNRs.** **a-c**, TEM images showing the process of ribbon formation: **a**, Li-BP crystal exhibiting unidirectional cracks (scale bar 250 nm); **b**, Li-BP demonstrating in plane splitting as ribbons are formed

(scale bar 250 nm), the full image is presented in Extended Data Fig. 8; **c**, composite micrograph of individualised PNRs following bath sonication (scale bar 1  $\mu\text{m}$ ). **d**, Schematic of the electrodeposition setup; patterned Pt on Si/SiO<sub>2</sub> as working (positive) and counter electrodes and a Pt wire quasi-reference electrode (offset in the direction of the page). The optical image shows the grid over which Raman mapping was performed following deposition, the lighter coloured region is the Pt coating on the green Si/SiO<sub>2</sub>. **e**, **f** the intensity of the fitted phosphorene A<sub>g</sub><sup>2</sup> and silicon peaks (scale bars 20  $\mu\text{m}$ ) on the electrode following plating. **g**, example Raman spectrum from PNRs drop-cast onto graphite (Methods).

## Methods

### Production of phosphorene nanoribbons

1. Intercalation of BP crystals Macroscopic BP crystals (Smart Elements, 99.998% purity) were first outgassed at 100 °C under dynamic vacuum ( $< 10^{-6}$  mbar) for one week. Without exposure to air, the outgassed crystals were loaded along with lithium metal (99.9% Sigma Aldrich) at a stoichiometric ratio of Li:8P, in a quartz reaction tube and attached via a glass-metal transition to a leak-tight, custom, gas-handling manifold. The tube was immersed in a propan-2-ol bath and the temperature cooled to, then maintained at, -50 °C using a Julabo FT902 chiller. High-purity ammonia gas (Sigma Aldrich  $> 99.99\%$ ) was then condensed onto the BP and Li, dissolving the alkali metal. The BP was left submerged in the dilute lithium-ammonia solution (concentration  $< 1$  mole percent metal) for 24 hours, during which time intercalation occurred. Following this process the ammonia was slowly removed by cryo-pumping, and the intercalated BP crystal was then further dried by vacuum treatment ( $< 10^{-5}$  mbar for 1 hour), before being removed to a high purity argon glovebox (O<sub>2</sub>, H<sub>2</sub>O  $< 0.1$  ppm).

Choice of alkali metal to BP ratio Attempts to intercalate BP with alkali metals are known to result in a mixture of products including un-intercalated BP, intercalated BP and alkali metal

phosphides<sup>8,26-28,32-38</sup>. Recently a careful experimental study of the relative concentrations of these reaction products, depending on the stoichiometric ratio of metal added to the BP (M:P), was reported<sup>26</sup>. This work, in which BP was intercalated via exposure to a sodium or potassium melt in an inert atmosphere, demonstrated that intercalation is always accompanied by some degree of phosphide formation, the relative concentration of which increases with increasing M:P ratio. Furthermore, successful intercalation of BP only manifests as a subtle change in the associated X-ray diffraction (XRD) pattern. Another recent BP intercalation study, using the same ammonia-based intercalation method employed here, again found no well-defined layer increases typical for intercalation compounds<sup>39</sup>. We also found that increasing the M:P ratio concomitantly increases the proportion of phosphides produced. If a stoichiometry of M:4P was used, PNRs were produced (following solvent addition) but alongside a large amount of debris/phosphides. However, decreasing the stoichiometry to M:16P significantly lowered the eventual yield of PNRs. A compromise of M:8P was therefore chosen, which produced a similar eventual ribbon yield to higher metal ratios while significantly reducing the phosphide/debris production. Sodium (99.95% Sigma Aldrich) intercalation, i.e. instead of using lithium, was also found to be effective at producing PNRs.

Characterisation of Li intercalated BP The lithium-intercalated BP (Li:P ratio 1:8) was investigated by Raman mapping experiments (experimental details below), the results are presented in Extended Data Fig. 8. Upon lithium intercalation, a number of new Raman peaks appear Extended Data Fig. 8a, b (top panels) similar to those reported for Na- and K-intercalated BP<sup>26</sup>. Also for the intercalated sample, there is a significant down shift of the  $A_g^2$  peak position from  $467\text{ cm}^{-1}$  in pristine BP<sup>40,41</sup> to  $462\text{ cm}^{-1}$  (mean) in the intercalated crystal (Extended Data Fig. 8d) though with a broad spread of values (standard deviation  $0.6\text{ cm}^{-1}$ )

indicating the doping is inhomogeneous. A similar downshift was previously observed for Na and K intercalation upon doping<sup>26</sup>. Extended Data Fig. 8f is a map scan of the  $A_g^2$  position for spectra taken in the red rectangle of the bottom panel in Extended Data Fig. 8c. The position of the  $A_g^2$  peak (indicating the extent of doping) is found to vary in stripes aligned in the same direction as the unidirectional features seen in the optical micrographs of Extended Data Fig. 8c. Raman mapping was performed in two sample orientations, with the stripes parallel and perpendicular to the incident laser polarisation. The orientation had a significant effect on the  $A_g^1/A_g^2$  peak intensity ratio (Extended Data Fig. 8e) with the ratio being notably larger with the laser polarisation parallel with the stripes ( $\sim 0.8$  compared with  $\sim 0.2$ ). The Raman spectra from pure BP are known to have a strong polarisation dependence, although it should be noted that the dependence is different for different sample thicknesses and laser wavelengths<sup>40-43</sup>. In particular, spectra of bulk BP indicate a  $A_g^1/A_g^2$  intensity ratio maximum for polarisation in the zigzag and minimum in the armchair direction<sup>42,43</sup>. Therefore, the peak intensity changes observed here imply that the doping stripes are parallel to the zigzag direction. This inhomogeneous and directional doping is consistent with the proposed mechanism and with in-situ experiments in Ref [27].

Finally, the Li-intercalated crystal was exposed to air and the measurements repeated (Extended Data Fig. 8a, b bottom panels) following similar experiments in Ref [26]. The Raman spectra show disappearance of the intercalation peaks so that only peaks of pure BP remain, with the  $A_g^2$  peak reverting to  $466.8\text{ cm}^{-1}$  (standard deviation  $0.1\text{ cm}^{-1}$ ), (Extended Data Fig. 8d). This data indicates that during air exposure the crystal de-intercalates.

A HS-AFM micrograph of the surface of the Li-BP crystal is presented in Extended Data Fig. 8h. The crystal surface shows a ribbon that is liberated from the surface of the crystal with a

corresponding ‘trench’ left behind, indicating that ribbon formation occurs during intercalation (Extended Data Fig. 1 step 5).

The colour change throughout the intercalation process is noteworthy. For most layered materials, during ion intercalation via the ammonia route, the originally deep blue solution (colour arising from the solvated electron) eventually turns colourless (pure ammonia) with the intercalated layered material left at the bottom of the container<sup>29</sup>. In the current work, an orange solution was always found above the intercalated crystal, presumably owing to the presence of phosphides, which are soluble in ammonia as previously reported<sup>37,38</sup>. The solubility of the phosphides in ammonia is beneficial since it allows the amount of this undesirable by-product to be decreased following intercalation.

2. Formation of PNR dispersions Within a high purity argon glovebox an anhydrous aprotic solvent (typically 1 mL) was added to the intercalated Li-BP crystal (typically 1 mg) in a glass vial. The vial was then sealed and placed in an ultrasonic bath (Ultrawave QS3, 50 W) for 1 hour; the bath water was changed every 20 minutes in order to keep the water temperature below 40 °C. Alternatively, stirring the Li-BP/solvent mixture using a glass coated magnetic stir bead for 1 week inside the glovebox was found to be equally effective, and produced PNRs that were indistinguishable (via TEM analysis) from those produced via 1 hr bath sonication. To remove larger stirred-up fragments of Li-BP crystals, low-g centrifugation was used at 385 g (2000 RPM) for 20 minutes (Hettich EBA 20). For the spontaneously dissolved sample (Extended Data Fig. 6), solvent was added carefully to Li-BP, so as not to disturb the powder and left for one week, before an aliquot was removed from the uppermost portion of the solution for analysis. A schematic representation of the PNR production process is shown in Extended Data Fig. 1.

445

446 The solvents that successfully produced stable dispersions of high-quality PNRs were all  
447 polar and aprotic, similar to those used to dissolve other charged nanomaterials, that is,  
448 chosen not to react with the charged nanomaterials but to permit thermodynamic  
449 dissolution<sup>29,44,45</sup>. Of the polar, aprotic solvents tested, n-methyl-2-pyrrolidone (NMP),  
450 dimethylacetamide (DMAc), dimethylformamide (DMF) and acetonitrile, produced ribbons,  
451 tetrahydrofuran (THF) and dichloromethane (DCM) did not. Of the effective solvents,  
452 DMAc, DMF and acetonitrile produced more concentrated ribbon dispersions (from TEM  
453 inspection), however, NMP dispersions contained a lower percentage of non-ribbon BP  
454 fragments and was therefore the solvent adopted during this work.

455

456 Attempts at PNR production were also made using the following solvents: IPA, acetone,  
457 water and hexane. These solvents were all ineffectual at producing ribbons. Hexane produced  
458 no dispersed material. IPA, acetone and water resulted in a mixture of short amorphous  
459 species and qualitatively shorter ribbons however, little crystallinity was evident from SAED,  
460 suggesting significant functionalisation or chemical reaction of the ribbons or the intercalated  
461 crystal.

462

463 Control experiments The procedure described above for forming PNRs was repeated for both  
464 BP crystals that had not been intercalated and BP crystals that had just been submerged in  
465 liquid ammonia (but with no metal present). In both cases, neither ribbon-like fragments nor  
466 any exfoliated (sheet-like) BP were found in TEM.

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468 **Deposition of PNRs onto substrates**

PNRs were drop-cast from solution in NMP onto freshly cleaved graphite (HOPG, GE Advanced Ceramics ZYH grade) or TEM grids (details below). NMP, though commonly used in processing of nanomaterials<sup>46</sup>, is a high boiling solvent with low vapour pressure that can also polymerise at high temperatures<sup>47</sup>, so its removal can be problematic. Therefore (unless stated differently) the following drying procedure was adopted to remove NMP from drop-cast substrates. The NMP solution was dropped onto the substrate in a high purity Ar glovebox ( $O_2$  &  $H_2O$  <0.1 ppm) using a micro-pipette. The substrate was then transferred (air-free) to a custom-built apparatus and subjected to Ar gas (BOC pureshield argon) flow for ~8 hours at room temperature. Without exposure to air, the substrates were then evacuated to  $10^{-6}$  mbar using a turbomolecular pump and left under dynamic vacuum (continuous pumping) for one week before the temperature was increased to 100 °C for a further week. The samples were then removed without exposure to air and stored in a high purity argon glovebox. Thus (unless stated otherwise) all deposited samples PNR samples investigated were kept in inert conditions for at least two weeks prior to experiment.

The drop-coated PNRs are not expected to be doped or intercalated with lithium ions for the following reasons: 1. All Raman spectra for Li-BP show strong downshift of the  $A_g^2$  peak and extra peaks (Extended Data Fig. 8a, b), which are absent from all spectra taken on deposited PNRs for which  $A_g^2$  is in its undoped position (Extended Data Fig. 9d); 2. The heights of the multilayer (1-5 layers) PNRs (Extended Data Fig. 4) closely match the layer heights expected for unintercalated BP, whereas intercalated ions are known via calculations and experiments to increase the out-of-plane lattice parameter by up to 20% (Refs 26,27); 3. Doped/intercalated BP is metallic<sup>26,39</sup> and therefore would not be expected to luminesce (Extended Data Fig. 9f). Strategies exist for removing residual alkali metals from SWCNT and graphene deposited from analogous solutions of their charged species<sup>48</sup>.

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495 XPS data taken over large areas (spot diameter 400  $\mu\text{m}$ ) of deposited PNRs on graphite  
496 (Extended Data Fig. 10h) could not detect the presence of any residual phosphides (within the  
497 limits of the measurement) which would appear as a peak at lower binding energies ( $\sim 129$   
498 eV) Ref [49].

499

500 Electrodeposition was performed using a custom-built three-electrode cell inside a high  
501 purity glovebox for 24 hours using a Gamry Interface 1000 potentiostat. A platinum wire was  
502 utilised as a quasi-reference electrode and the counter and working (positive) electrodes were  
503 formed of oxidised silicon wafers that were partially coated with Pt (PI-Kem). The deposition  
504 was undertaken at a static potential of 1.1 V, which was held for 24 hours. For electroplating  
505 we used DMAc as a solvent to minimise solvent decomposition products.

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#### 507 **Stability of PNRs in solution and in air**

508 To investigate the stability of the PNRs in solution, we monitored the UV/Vis absorption  
509 spectrum of the solution over 50 days similar to studies in Refs [50,51]. The UV/Vis  
510 absorption spectrum of PNRs in NMP (Extended Data Fig. 9g) is qualitatively very similar to  
511 that of liquid dispersions of BP nanosheets<sup>50</sup>, i.e. showing increased absorbance at lower  
512 wavelengths and small features below 500 nm (Refs 50,52). The relative change in  
513 absorbance at 465 nm over 50 days was fitted with an exponential decay function following  
514 the analysis outlined in Refs [50,51] (Extended Data Fig. 10i). In these references, the  
515 decrease in absorbance over time is attributed to the dispersed BP nanosheets gradually  
516 degrading into reaction products that do not absorb in this spectral region<sup>50</sup>. Therefore, from  
517 the empirical fit, the decay constant and the unreacted fraction of pristine BP that remains can  
518 be extracted. For our charged PNRs in NMP, measured in inert conditions, we find a



significantly greater unreacted fraction ( $98.5 \pm 0.4 \%$ ) than the equivalent optimal case for BP nanosheets dispersed in deoxygenated CHP in inert atmosphere. Moreover while the researchers in Ref [50] shake samples before each measurement to ‘avoid sedimentation effects’, in contrast, we took care not to disturb our PNR solutions between measurements, in order to establish whether or not sedimentation occurs. The comparatively small decrease in absorbance therefore also demonstrates that the PNR dispersions are stable against flocculation. This stability is expected since the PNRs spontaneously dissolve (Extended Data Fig. 6) because they are charged<sup>29,44,45</sup>. Reaction with residual water/oxygen in the solvent could account for the small decrease in absorbance observed over the 50 days.

Though PNRs were found to be stable in inert conditions, BP is well-known to be air-sensitive with an increasing instability to oxidation as the number of layers are reduced, though the exact details of the mechanism are currently under debate<sup>43,53-56</sup>. We therefore studied the effect of increasing air exposure on PNRs deposited onto HOPG substrates drop-cast from the same solution using XPS, Raman spectroscopy and HS-AFM. The relative humidity was monitored to be ca. 50% over the course of the experiment.

Following air exposure AFM measurements on BP typically reveal a marked increase in surface roughness due to water adsorption<sup>43,53,54</sup>. This process causes rapid further degradation and fragmentation of the BP crystal<sup>43,53,54</sup>. We used HS-AFM to monitor changes in height and width of the same 1 and 2 layer PNRs over 6 days Extended data Fig. 10a-f. In contrast to 2D BP studied in air<sup>43,53,54</sup> we measured no significant change in height over the 6 days. However, we did measure a narrowing of the ribbons’ width, discernible after 6 days in air for both 1 and 2 layer PNR, (Extended Data Fig. 10a-f, method detailed below). The edge erosion for the PNRs exposed on a surface is similar to that recently measured (and

previously predicted<sup>50</sup>) for few layer BP if it is fully submerged in water in order to stop droplet build up on the surface<sup>55</sup>.

Raman studies of BP have consistently noted a decrease in  $A_g^1/A_g^2$  integrated intensity ratio with increasing air exposure, which has been demonstrated to be a metric for monitoring degradation on mechanically exfoliated phosphorene<sup>43,53</sup>. We therefore performed Raman mapping measurements on PNRs deposited on HOPG substrates over 6 days of air exposure (experimental details below). The air free PNRs have an  $A_g^1/A_g^2$  ratio of  $0.27 \pm 0.02$ , (Extended Data Fig. 9e) consistent with single/few layer BP<sup>40,43,53</sup>. However, unlike 2D phosphorene, with increasing air exposure, the average value of the  $A_g^1/A_g^2$  integrated intensity ratio does not change as a function of time (Extended Data Fig. 10g). On the other hand, the  $A_g^2$  peak:background ratio decreases monotonically (Extended Data Fig. 10g) indicating the degradation of the PNRs<sup>53</sup>. We also found a gradual decrease in average width and energy of the  $A_g^2$  peak over the 6 days (Extended Data Fig. 10g). This trend could be explained by the monolayer PNRs degrading at a faster rate than the multilayer PNRs since for 2D BP the  $A_g^2$  mode is known to both narrow and soften with increasing number of layers<sup>53</sup>.

XPS data of fresh and air exposed PNRs are plotted in Extended Data Fig. 10h. Similar to both bulk BP<sup>57</sup> and 2D few layer BP<sup>58</sup>, the PO<sub>x</sub> contribution (broad peak at ~134 eV) increases gradually over time. Though it should be noted that few/monolayer phosphorene is less air-stable than multilayer/bulk BP<sup>54</sup>. Eventually after 6 days the P-P contribution at ~130 eV becomes unmeasurable. The PO<sub>x</sub> contribution for the ‘fresh’ PNRs (2 – 5 minute air exposed during transfer to the spectrometer) is 15% of the total area, which the same as that reported for few layer phosphorene sheets created through liquid exfoliation methods<sup>50</sup>. Here

the surface sensitivity of XPS should be highlighted, as while the PNRs that are isolated or at the surface of collections of PNR oxidise, multilayer PNRs or those buried underneath are protected, evident from the Raman response even after 6 days.

Overall, the data show that PNRs are similarly susceptible to oxidation as few layer BP but the accelerated decomposition following water adsorption is significantly less pronounced, which perhaps explains a much slower fall off of the  $A_g^1/A_g^2$  intensity ratio with air exposure. Here, it should be noted that there are many methods that have been devised specifically to protect BP flakes from air during processing, as summarised recently<sup>54</sup> typically by liquid<sup>43,50</sup> or solid capping<sup>54</sup> that could be used to protect PNRs during processing.

## **Electron microscopy**

TEM samples were made by drop casting ribbons from dispersion onto holey/continuous carbon 200 or 300 mesh Cu or Au TEM grids (EM Resolutions). TEM was performed on a Jeol JEM 2100 equipped with a LaB<sub>6</sub> source operated at 200 kV. During transfer to the TEM chamber, the grids were exposed to air for approximately 2 minutes for mounting in the holder and ~5 minutes for evacuating the holder before insertion in the microscope. Specifically for EELS spectroscopy (Extended Data Fig. 3l, m) PNRs were drop-cast inside an Ar atmosphere glovebox on C-flat TEM grids that were heated to 80 °C for solvent evaporation. They were then transferred to the TEM as noted above with minimum exposure to air. The electron microscopy was performed on a double spherical aberration corrected ThermoFisher Scientific™ Titan Themis 60-300 operated at 60 kV. Electron energy-loss spectroscopy (EELS) was performed with a Gatan GIF Quantum™ spectrometer using the Gatan ADF STEM detector. The monochromator was excited and a 0.3 eV energy resolution

was achieved. All spectrum images (SI) were collected using Gatan DigitalMicrograph™ with a camera length at 29.5, giving a beam convergence semiangle of 26 mrad, a collection semiangle of 19.8 mrad, and an ADF inner detection angle of 41.2 mrad. Spectrum imaging was performed in dual EELS mode and data were acquired at 0.1 eV/channel dispersion. Typically, spectra were collected from areas of 200 x 50 nm<sup>2</sup> that were at the edges of the carbon support in order to avoid interfering signal from the carbon substrate. Still, signal from the low-loss, broad peak at 5 eV stemming from amorphous carbon was visible in the spectra. Finally, it is noted that core-loss probing of the oxygen K edge showed no oxidation of the sample.

To assess the distribution of ribbons within a sample, the TEM grids were randomly sampled over each quarter of a TEM grid. Around each randomly selected position, an area of 56 μm<sup>2</sup> (7.5 μm x 7.5 μm) was explored since multiple frames were required to image individual PNRs with sufficient resolution to measure their width along their length. Ribbon dimensions were measured using Gatan Digital Micrograph software. As can be seen from TEM figures from continuous carbon grids (Fig 1b, Fig 1d) as well as PNRs, the grids show there are an amount of small debris, most likely phosphides or small fragments of BP that have been produced during intercalation or sonication.

It is noted that degradation of the ribbons after electron beam exposure occurred in both 60 kV and 200 kV after several minutes. The electron dose rates, primarily responsible for the amorphisation of the ribbons, were kept low to preserve the integrity and crystallinity of the ribbons during data acquisition.

Composite TEM micrographs (Figs. 1, 3, and Extended Data Fig. 2 and 3) were constructed by superposing two or more overlapping images and are demarcated by dashed lines.

The crystallographic orientation of the ribbons was determined by indexing SAED patterns. Indexing was performed using Gatan GMS 3 software by comparing measured spot distances to the simulated TEM diffraction pattern from the crystal structure of BP. The orientation of this pattern reveals the real-space orientation of crystal planes and therefore the crystallographic alignment.

#### **High-Speed Atomic Force Microscopy (HS-AFM)**

Large area, high-resolution topography maps were generated using a contact-mode HS-AFM (Bristol Nano Dynamics Ltd, UK) as used in previous studies on solution deposited nanomaterials<sup>29,59,60,61</sup>. This instrument permits the rapid acquisition of data across areas thousands of square microns in size with sub-nanometre height resolution. The typical image size used in this work was 2 x 2  $\mu\text{m}$ , corresponding to a pixel size of 2 x 2 nm, and data were collected at a rate of 2 frames per second. Contact-mode silicon nitride cantilevers (Bruker MSNL, tip radius 2 nm nominal, 12 nm max) were used throughout.

HS-AFM samples were prepared by drop casting onto freshly cleaved graphite (HOPG) substrates. The substrate consists of large flat regions bounded by graphite step edges ranging from a single atomic layer to many tens or hundreds of layers high. To ensure that HOPG step edges were not miscategorised as PNRs, a user-guided analysis routine was implemented. First, the position and orientation of any PNRs within the candidate HS-AFM frame were identified, after which the analysis of their height and width was passed to an automated algorithm. Using custom software written in LabVIEW (National Instruments),

identified PNRs were highlighted by drawing a rotated rectangular region of interest. The region of interest was then extracted from the raw HS-AFM data using a local thresholding routine in order to identify the PNR against the HOPG background and produce a binary mask of the ribbon (1) and the HOPG background (0). This binary mask was then duplicated, with one copy being dilated (expanded) with two iterations of a 3 x 3 structuring element (to include the edges where the PNR touches the HOPG) and the other eroded (reduced) by two iterations (to exclude these same edges). These erosion and dilation steps ensure that the two masks exclude the transition region between the HOPG and the top of the PNR and prevent the inclusion of edge pixels where accurate categorisation as either an HOPG or PNR pixel is difficult. The resultant binary masks were then used to isolate the HOPG background and the top of the PNR respectively. Once isolated, the median of the HOPG background and PNR pixel heights were calculated and the difference used to classify the layer thickness for each pixel in the ribbon mask. The mean height of the background for all measurements was set to zero. For determination of the heights and roughnesses of 1-5 layer PNR, as presented in Extended Data Fig. 4, the number of individual pixel-height measurements (taken over multiple locations, PNRs and substrates) are: HOPG substrate (886,908 measurements); and for PNRs of 1 layer (61,181 measurements), 2 layer (50,637), 3 layer (18,740), 4 layer (78,514) and 5 layer (28,816). Though such step height measurements are highly sensitive to uncertainty (noise) this uncertainty is random, not systematic. As such it broadens the Gaussian distribution of step heights measured but does not affect the mean of the distribution. The result is an average height of the PNRs independent of signal-to-noise absolute values, provided a suitably large number of measurements are performed. In each case the extracted roughnesses,  $\sigma$ , are given by the standard deviation from the Gaussian fit to the associated height histograms, following the methods described in Lui *et al.*<sup>62</sup>.

This same software was used to track the edges of the PNRs and measure their widths along their lengths (Fig. 2c, d). The neutral or central axis of each PNR was calculated by fitting a cubic spline to both tracked edges and then calculating the mean path from these two fits. The distance from each edge to the neutral axis was then determined. This facilitates the calculation of a bulk mean width and standard deviation but does not evaluate the line edge roughness (LER) or line width roughness (LWR)<sup>59,63</sup>.

For the 75  $\mu\text{m}$  single PNR (Fig. 2e), the data was taken while manually tracking the PNR in real time. To create the composite image overlapping frames were offset by the difference in the median pixel value in their respective regions of overlap. Then, the newer frame was used to overwrite the data in the overlap region. Due to the high signal-to-noise ratio, there was no need to perform any image averaging. In this way, a consistent signal-to-noise was preserved regardless of the number of frames overlapping a given area. The XY position of each frame was recorded with nm resolution by the long-range positioners (SmarAct, Germany) used to pan the HS-AFM image window across the sample surface. This information was used to arrange the HS-AFM frames into their approximate locations. Final adjustments to the offsets between frames were carried out manually to account for drift of the sample relative to the positioners. The very high aspect ratio of this PNR meant that the typical methods used to present AFM data were unsuitable. Since the PNR traverses many HOPG steps tens of nm in height (but is itself less than 3 nm high for much of its length) it required a large dynamic range to visualise properly. To supplement the composite height map of this PNR and improve readability, a gradient image of the same region was calculated. The gradient image accentuates the surface texture by reducing the dynamic range of the image, aiding the display of nanoscale features present on large background slopes in the same way as the error/deflection image generated during conventional contact-mode AFM. The gradient

image was calculated from the composite height map along the fast scan direction using a five pixel moving window. The magnitude of the gradient was selected for display in Fig. 2e to give the PNR greatest contrast against the HOPG steps and background.

To analyse the distribution of PNR layer thicknesses (Fig. 2b), the HS-AFM was set to automatically image a 300 x 300  $\mu\text{m}$  region in the centre of an HOPG surface. A raster scan translated the HS-AFM image window across the full 300 x 300  $\mu\text{m}$  area and the resultant dataset was analysed using the same user-guided routine as described above.

For the air stability study, PNRs from the same location Extended Data Fig. 5e, f were measured over a six-day period (Extended Data Fig. 10a, d). Measurements were performed as detailed above, however an additional calibration step was included to determine the shape of the imaging tip of the AFM cantilever before each scan. This was performed to ensure that any observed changes in the height or width of the PNRs could be correctly attributed to real variations in the ribbons, rather than arising from tip convolution effects<sup>64</sup>, which may change over the different days. To achieve this, a HOPG trench on the same sample was imaged, this trench is expected to remain stable throughout all measurements as HOPG is not sensitive to atmospheric conditions. As such, any variation in the measured width of the trench can be attributed to fluctuations in the shape of the imaging tip arising from picking up contaminants from the sample surface during scanning, or wear of the tip itself. The HOPG trench was therefore used to correct for the effects of tip sharpness variance.

#### **Optical characterisation.**



Raman and PL spectra were collected using a Renishaw In-Via microscope equipped with a 488 nm laser through an x20 objective. For the Raman spectra of plated and drop-cast PNRs, Li-BP and the PL experiments, the samples were contained in argon environment in a custom made glass cell. For the air-free Raman measurements (Fig 3, Extended Data Fig. 9), air exposure (Extended Data Fig. 10) and PL measurements samples were dropped onto freshly cleaved HOPG from the same solution and the maps taken over high local concentrations of PNRs to measure their collective optical properties. For the air-free Raman spectra, 351 spectra from a 15  $\mu\text{m}$  x 25  $\mu\text{m}$  grid were fitted with 3 Lorentzian functions between 350 and 500  $\text{cm}^{-1}$ , using a custom implementation of the Levenberg-Marquardt algorithm and the positions, intensity and widths extracted. These data were then used to create histograms of the positions and widths and the relative intensities across the map, from which Gaussian fits (Extended Data Fig. 9) were used to extract average positions and standard deviation of these distributions. For the air exposure experiments the same area was probed, though on a less dense grid of between 90-100 spots and with shorter counting times in order keep each overall map acquisition to below 2 hours. For the plating measurements the map scan of the positive electrode (Fig. 3c) - spectra from 255 points on an 80  $\mu\text{m}$  x 70  $\mu\text{m}$  grid were measured, and each was fitted with Lorentzian line-shapes in the window for the BP peak at 467  $\text{cm}^{-1}$  and silicon peak at 520  $\text{cm}^{-1}$ . Equivalent data were taken from the counter electrode and showed no preferential PNR deposition. For the Li-BP crystal measurements, the four maps were taken over the same region of the crystal surface with the polarisation of the incident laser perpendicular or parallel to the vertical features in the optical image. Spectra from the Li-BP crystal were fitted with 8 Lorentzian functions as shown in Extended Data Fig. 8a, b. PL spectra were recorded with a 1200 line/mm diffraction grating (as opposed to 2400 lines/mm for Raman spectra), using a long-pass filter (cut-on wavelength 700 nm) for

the low energy ( $< 1.74$  eV) part of the spectrum to remove peaks originating from second order diffraction on the grating.

Optical absorption spectra were measured on a Shimadzu UV-2600 spectrometer equipped with an ISR2600Plus integrating sphere attachment in a 4 mm path length quartz cuvette. To maintain an inert atmosphere the cuvettes were filled in the glovebox and sealed. A background of pure solvent loaded in the same cell was subtracted from the spectra.

#### **XPS measurements**

XPS spectra were acquired using Thermo Scientific K-Alpha (mapping study) and Theta Probe (oxidation study) spectrometers, both fitted with a monochromated Al  $K_{\alpha}$  sources (1486.6 eV). The P 2p spectra were fitted with mixed Gaussian/Lorentzian peaks (spin-orbit ratio 1:2, 1/2: 3/2; peak separation 0.86 eV), a single Gaussian/Lorentzian was used to fit the oxide peak due to the broader nature of oxide-derived spin-split core levels. XPS mapping was performed over areas of  $\sim 5$  mm<sup>2</sup> using a beam size of 400  $\mu\text{m}^2$  and step sizes of 400  $\mu\text{m}$ . The doublet of peaks at  $\sim 130.5$  eV can be assigned to the P-P environment (P-O at  $\sim 134$  eV) (Ref 57) and the integrated area under this peak pair was used to construct the maps. For the oxidation study, PNRs were dropped onto freshly cleaved HOPG in a low oxygen glovebox, dried as described above, then exposed to atmosphere for increasing periods of time.

#### **Supplementary references**

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**Data availability** The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

**Extended Data Fig. 1 | Schematic of PNR production.** BP crystals were outgassed in a quartz reaction tube (1) and lithium metal was added (2). The tube was cooled to -50 °C and

high-purity ammonia was condensed onto the BP and Li (3), dissolving the alkali metal to form a Li:NH<sub>3</sub> solution. The BP was then left submerged in the Li:NH<sub>3</sub> solution for ~24 hours, allowing intercalation (4), before the ammonia was slowly removed. Without air exposure, the intercalated BP crystal was transferred to a glovebox and placed into a vial (5) and NMP was added (6). This vial was then placed in an ultrasonic bath for 1 hour and centrifuged at low-g. This process resulted in solutions of PNRs (7).

**Extended Data Fig. 2 | Gallery of PNRs.** TEM micrographs showing PNRs (darker ribbon-like features) deposited on ‘holey-carbon’ TEM grids (lighter webbed structure). **a**, Heterogeneous PNRs of different widths. **b**, Micrographs of high aspect ratio (> 100) PNRs with widths < 5 nm. Dashed boxes mark areas where a zoomed (and therefore higher resolution) overlay has been superposed, solid boxes correspond to the extracted zoom insets. To enhance visibility select PNRs have been outlined by dashed lines, otherwise, red arrows indicate the location of the ribbon. **c**, Images of PNRs that demonstrate their flexibility. Composite TEM images are demarcated by dashed, black boxes.

**Extended Data Fig. 3 | Electron microscopy, diffraction and spectroscopy of individual PNRs.** **a-f**, SAED patterns (scale bar 10 nm<sup>-1</sup>) taken at the locations corresponding to the boxes marked in the composite TEM image in **g** (scale bar 1 μm). These images show the zigzag crystallographic alignment along the length of the PNR, indicated by the red arrows. **h**, indexed FFT transform (scalebar 10 nm<sup>-1</sup>) of the HRTEM micrograph shown in Fig 1h. **i**, STEM (scalebar 2.5 μm) and **j**, TEM (scalebar 2 μm) images of the same PNR for which EEL spectra (**l,m**) were recorded. **k**, closer view (scale bar 1 μm) of PNR shown in **i** (left), and spectrum image chosen at a suspended-in-vacuum part of the ribbon (right) indicating as a red square the region from which EEL spectra shown in **l** & **m** were averaged. **l**, Core-loss EELS at the P L<sub>2,3</sub> edge (130 eV) showing features in regions I, II and III that correspond to features found in pristine few layer BP<sup>31</sup>. **m**, low-loss EELS spectrum showing the expected plasmonic signature peak at ~19 eV and another feature at ~3.3 eV similar to that found for few layer BP and attributed to surface plasmons<sup>31</sup>. The broad feature at ~5 eV marked with an asterisk is from delocalized signal coming from the amorphous carbon support.

**Extended Data Fig. 4 | Heights and roughnesses of 1-5 layer PNRs from statistical analysis of HS-AFM images (Methods).** Normalised histograms (black error bars) and Gaussian fits (solid blue line) of independent, automated, pixel-height measurements from the HOPG substrate (far left curve) and for PNRs of 1 - 5 layers. The extracted average heights (z) and roughness (σ) are shown above each ribbon. Scaled representations of the crystal structures of 1-5 PNRs are overlaid.

**Extended Data Fig. 5 | HS-AFM of PNRs.** **a**, a zoom of the PNR from Fig. 2e (scale bar 5 μm). **b** zoomed image of the bifurcation found in **a** (scale bar 500 nm). **c**, **d** linecuts taken from **b**, before (**c**) and after (**d**) the bifurcation, that demonstrate the ribbon self-cleaves from its original height of ~3.5 nm (7 layers) to two branches of heights ~1.5 nm (3 layers) and ~2

nm (4 layers). **e, f**, HS-AFM images (scalebars 200 nm, 500 nm respectively) of areas over which the stability study presented in Extended Data Fig. 10a-f was taken. In **e**, black box corresponds to HOPG trench used to correct the stability data for tip effects (Methods) and blue box corresponds to bilayer PNR in Extended Data Fig. 10d. In **f** the blue box corresponds to the monolayer ribbon presented in Extended Data Fig. 10a.

**Extended Data Fig. 6 | Dimensions of spontaneously dissolved PNRs.** Length vs width scatter plots of dispersed PNRs extracted from TEM data (Methods). The plot shows the PNRs that have spontaneously dissolved from Li-BP crystals into NMP solvent (red circles) as well as those formed via bath sonication (blue circles). The zoom (right) corresponds to the dashed rectangle on the left-hand image and reveals that the spontaneously dissolved PNRs are wider than those formed by sonication.

**Extended Data Fig. 7 | XPS and Raman spectroscopy of electrodeposited PNRs.** **a**, XPS maps of the patterned-Pt positive (left), and negative (right) terminal electrodes from PNRs electrodeposition. Maps were constructed from the integrated area under those P 2p peaks assigned to the P-P environment (scale bar 500  $\mu\text{m}$ ). **b**, Schematic representations of the Pt pattern (grey) on the positive (left) and negative (right) electrodes. **c**, an example P 2p spectrum from, **a**, fitted with mixed Gaussian/Lorentzian peaks assigned to P-P bonding and P-O surface contamination. **d**, patterned electrode showing grid over which Raman maps presented in Fig. 3e, f were taken (scale bar 20  $\mu\text{m}$ ). The blue and red dots in **d** show the specific locations where the example Raman spectra shown in **e**, were taken.

**Extended Data Fig. 8 | Characterisation of lithium intercalated-BP.** **a, b** Example Raman spectra of Li-BP recorded with the incident laser polarisation perpendicular to (**a**) or parallel (**b**) to the vertical features in **c** (bottom). The top two spectra of (**a**) and (**b**) are performed in argon, the bottom two after 30 days in air from the same region in the sample. These spectra are fitted (Methods) with a sum (red curve) of Lorentzian functions for BP (blue curves) and intercalation (green curves) Raman modes. **c**, optical micrographs of a Li-BP crystal top (scalebar 200  $\mu\text{m}$ ), and bottom zoomed in (scalebar 18  $\mu\text{m}$ ). The bottom image also shows the area (dashed box) over which the Raman mapping data presented in **f** were taken from. **d**, histograms of the positions of Li:P  $A_g^2$  peak position in argon (orange) and after 30 days in air (green). **e**, histograms of the  $A_g^1/A_g^2$  peak intensity ratio for measurements performed with the incident laser polarisation parallel (blue) or perpendicular (yellow) to the vertical stripes in **c**. **f**, map of the position of the  $A_g^2$  peak for data taken over the red box in **c** (scalebar 5  $\mu\text{m}$ ). **g**, TEM image showing in-plane splitting of PNRs from a larger fragment (scalebar 500 nm). **h**, HS-AFM image (top, scalebar 100 nm) and associated linescan (bottom) of the surface of an Li-BP crystal showing a ribbon (line profile 1, black data) liberated on the surface and the trench left behind (line profile 2, red data).

**Extended Data Fig. 9 | Collective optical properties of PNRs.** **a**, Example Raman spectrum (black circles) taken from PNRs deposited on a graphite substrate in an argon atmosphere (Methods). The spectrum is fitted with a sum (red curve) of three Lorentzian functions (blue curves) corresponding to the  $A_g^1$ ,  $B_{2g}$  and  $A_g^2$  peaks of black phosphorus<sup>40,41</sup>. **b-d** histograms

of the positions (top) and widths (bottom) of the Raman modes and, **e**, the integrated intensities ratios of the  $A_g^1:A_g^2$  peak (top) and the  $B_{2g}:A_g^2$  peak (bottom), extracted by fitting 351 independent spectra taken from the same sample of solution-deposited PNRs. From the fits to the distributions in **b-d** the mean values and the standard deviations, given in brackets, of the Raman peak positions and widths were determined to be:  $A_g^1$  position  $362.5 (0.2) \text{ cm}^{-1}$ , width  $3.3 (0.2) \text{ cm}^{-1}$ ;  $B_{2g}$  position  $439.3 (0.2) \text{ cm}^{-1}$ , width  $5.4 (0.3) \text{ cm}^{-1}$ ;  $A_g^2$  position  $467.5 (0.2) \text{ cm}^{-1}$ , width  $3.7 (0.2) \text{ cm}^{-1}$ . **f**, PL spectrum from PNR aggregates deposited on graphite, peaks at high energy are Raman features from the PNR or the graphite substrate (the latter marked by asterisks). Mechanically exfoliated single layer phosphorene emits at  $\sim 1.3 \text{ eV}$  (Ref 65). **g**, UV/Vis absorption spectra from a PNR solution (inset), the red circles mark the positions of weak features below 500 nm.

**Extended Data Fig. 10 | Stability of PNRs.** **a**, HS-AFM images (scalebars 50 nm) of the monolayer PNR shown in Extended Data Fig. 5f taken immediately (top) and following 6 days air exposure (bottom). **b**, histograms of the width (left) and height (right) of the PNR in **a** taken immediately (blue) and after 6 days in air (yellow), each histogram has been fitted with a Gaussian function (red). **c**, the width (left) and height (right) of the PNR over 6 days in air taken from fits to histograms as shown in **b**. **d**, HS-AFM images (scalebars 50 nm) of the bilayer PNR shown in Extended Data Fig. 5e. **e-f**, the equivalent data as described in **b-c** but taken for the bilayer ribbon in **d**. **g**, evolution of the Raman  $A_g^1:A_g^2$  integrated intensity ratio, the  $A_g^2$ :background intensity ratio,  $A_g^2$  position and  $A_g^2$  width (top to bottom respectively) extracted by analysing maps of 90-100 independent spectra taken over the same location from a sample of PNRs drop-cast onto graphite (Methods). **h**, evolution of XPS spectra (data black dots, red curve fits to P peaks, blue curve fits to P-O peaks) taken from a sample of PNR drop-cast onto graphite as a function of increasing air exposure (top to bottom). **i**, Normalised absorbance at 465 nm (black dots) as a function of time taken from the same solution of PNR in NMP (photograph shown in inset) over 50 days without exposure to air. Red curve is an exponential function fit to the data (Methods).







